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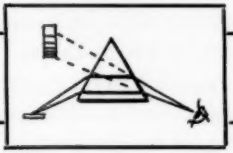

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OPTICAL METHODS FOR REDUCING THE EFFECTS OF PHOTOGRAPHIC PLATE GRAININESS. WITH SPECIAL REFERENCE TO SPECTRAL LINE AND STAR IMAGE MEASUREMENTS

By F. E. Wright.
[Geophysical Laboratory, Washington, D. C.
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Photographic plates are widely used in astronomy and allied sciences for recording images on which position measurements are to be made. In high speed plates the effects of coarse grains (clumps and aggregates of minute crystals) are serious because the observer is likely to place undue emphasis on a coarse grain in making his measurement. To diminish the obtrusiveness of the coarse grain he resorts commonly to a lower magnification than he prefers. Fine-grained, high speed photographic plates are not yet available. In the meantime any method that decreases the effects of plate graininess and tends to increase contrast is useful.

Spectral Lines

Spectral lines are straight and parallel. This fact serves as the basis for a number of different methods for fusing the lines. These methods may be classed into the following groups:

(a) The image of the spectral lines is made to oscillate rapidly in the

direction of the lines. Each spectral line is thus integrated into a continuous line (Method of Linnik).

(b) Each plate grain is imaged as a dark line by means of a cylindrical lens placed above the objective with its axis normal to the spectral lines. The series of overlapping lines, thus produced, blends into a grainless, continuous spectral line (Method of Anderson).

(c) A thick plate of glass with plane parallel sides is placed between the objective and the negative and is tilted at a steep angle with the line of sight and in the azimuth of the spectral line. Astigmatism and coma are hereby introduced and spread the object points into short image lines which overlap to form a continuous spectral line.

(d) Reduce the resolving power of the observing system, either by use of a narrow slit diaphragm in the rear focal plane of the objective or by the minification-magnification method, so that in the image the points along a spectral line are no longer separated.

(e) Place a Wollaston prism on the negative and produce two overlapping images of a spectral line. The number of the grains along the line is thus doubled and satisfactory fusion is obtained for many types of lines.

(f) Viewed under dark ground illumination each spectral line becomes a series of illuminated points and appears as a light line on a dark field. In certain cases it is easier to make an accurate setting on this line after fusion by one of the above methods than on the original dark line.

These different methods will now be considered briefly and their effects on the resulting image compared. The tests show that the character of the image illumination differs from method to method, and that one method is better for one type of spectral line and another method for another type. No one method is greatly superior to the others.

(a) *Vibrating image.* (1) In 1930 W. Linnik[1] described a method for producing an image that oscillates in the direction of the spectral lines. The microscope objective is screwed into a ring suspended by two short arms on knife edge supports from a ring attached to the microscope tube. The combination is free to swing, like a pendulum, and the image oscillates to and fro in front of the eyepiece. A thin plano-concave lens is placed with its flat surface over the negative to compensate the change in focus caused by the changes in position of the objective. By this method each grain is elongated into a line whose length depends on the amplitude of vibration of the objective; the intensity of the line is

[1] ZS f. Physik, *61*, 700–702; 1930.

greatest at the two ends. A heavy field grain may produce a spurious line which, however, decreases in length as the amplitude of vibration becomes less. The frequency of vibration is relatively slow but constant. Care should be taken to align the plane of vibration with the elongation of the spectral lines. By this method the field grain disappears and the spectral lines become solid lines on which accurate measurements can be made.

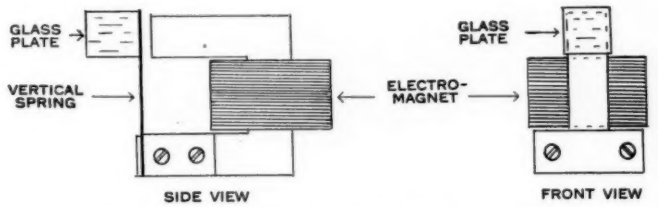

FIG. 1. *Sectional views of glass cube mounted on an elastic steel spring driven by an electromagnet on an alternating current to produce rapid oscillations in the image of a spectrogram.*

(2) Another method for producing an oscillating image whose frequency of vibration can be changed consists in cementing a small cube of plate glass to a vertical flat spring mounted on a support (Fig. 1) and placed between the objective and the negative. The glass cube can be set vibrating with a frequency that depends on the length and stiffness of the spring and on the mass of the glass plate. Instead of starting the vibration by hand, a small electromagnet actuated by a rapidly alternating current can be used with a short flat spring, properly adjusted to resonance, to produce very rapid oscillations.[2] With a 60-cycle alternating current the oscillations are too rapid for the eye to detect. The result is a clear, steady field and well fused spectral lines (Fig. 2B; Fig. 2A is an unmodified copy of an iron-arc spectrogram). The amplitude of vibration can be increased up to several millimeters by placing the pole piece of the electromagnet near the vibrating spring. The effect of rocking the glass plate is to cause the image to shift back and forth. At the inclined position, the tilted plate introduces an effect of coma and astigmatism into the image points along the spectral lines and this aids in the fusion to homogeneous lines. The plane of vibration should be placed accurately parallel with the spectral lines. In place of the glass cube a weak lens, either positive or negative, can be substituted; a spectacle lens of one or two diopters is satisfactory. With this arrange-

[2] The suggestion to use an electromagnet for this purpose was made by Mr. H. S. Roberts of this Laboratory.

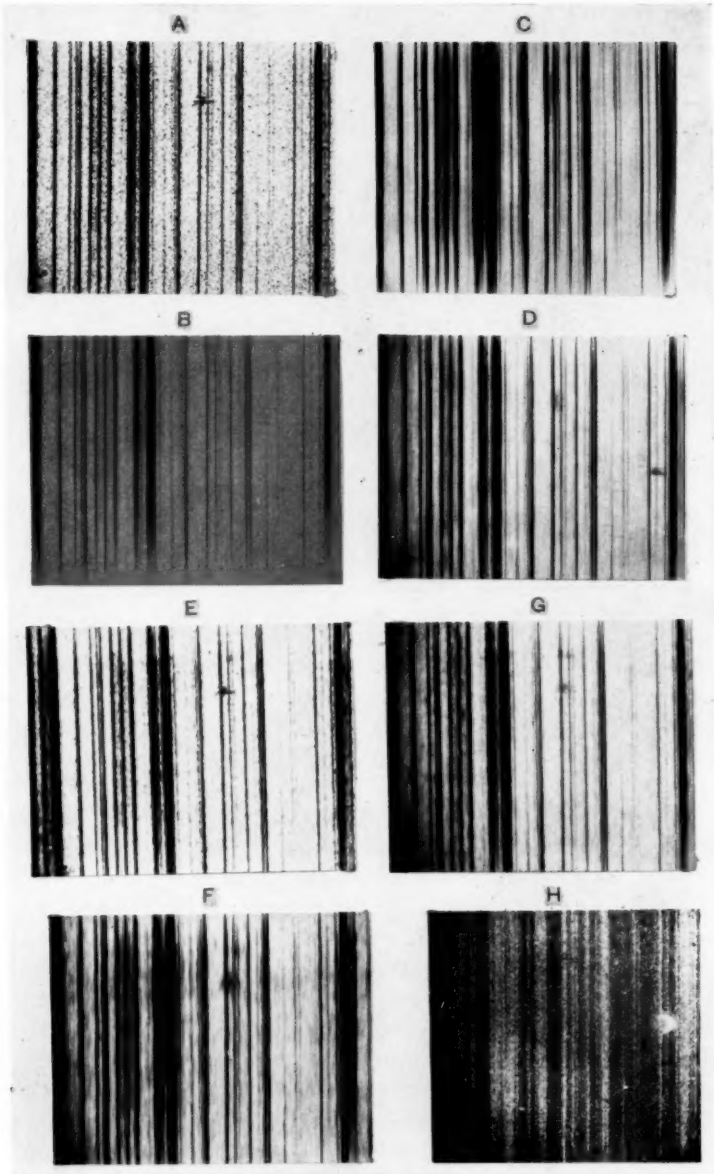

FIG. 2. *Photomicrographs (magnification 23 X) of an iron-arc spectrogram to show the effects produced by different methods for eliminating photographic plate graininess from the spectral lines. Fig. 2A is a copy of the unmodified spectrogram. The remaining photomicrographs illustrate the character of the fusion produced by: the vibrating glass cube (Fig. 2B); the cylindrical lens (Fig. 2C); the tilted glass plates (Fig. 2D); two slit diaphragms of different apertures (Figs. 2E, 2F); the Wollaston prism (Fig. 2G); dark ground illumination (Fig. 2H).*

ment the spring may be used in a horizontal position and the method can be employed with a higher power objective than is possible with the glass cube.

(3) A more complicated but effective method of rocking the plate through any given angle and at any given speed is illustrated in Fig. 3. A small, massive flywheel is set rotating either by hand or by a small

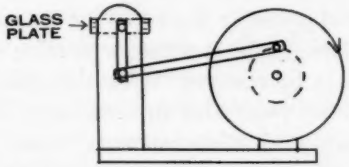

FIG. 3. *Section of apparatus for rocking glass cube to produce vibrating image.*

electric motor. A connecting rod, attached to a pin on this wheel, transmits its motion to an arm extending from the horizontal axis on which the glass plate is mounted and about which it is rocked. Although the frequency of oscillation obtainable by this method is less than that of the preceding method, it is adequate and in certain cases the greater amount of tilting may be an advantage.

(b) *The cylindrical lens method.* This method was first applied by Dr. J. A. Anderson of Mt. Wilson Observatory.[3] A planocylindrical lens of suitable focal length is inserted, with its axis normal to the spectral lines, above the objective of the observing microscope. A line image of each point in the photographic plate is thereby produced, thus integrating the grains along a spectral line to a solid line (Fig. 2C). Normal to the spectral lines the cylindrical lens (along its axis) does not magnify and the widths of the spectral lines and their separations remain unchanged. The length of the linear element thus produced from a plate grain can be decreased by shifting the position of the cylindrical lens away from the objective and toward the eyepiece. If the focal length of the cylindrical lens is too short, the length of the image line corresponding to a plate grain is excessive and each prominent grain gives rise to a spurious spectral line that may be disturbing. To distinguish a spurious line from a spectral line rotate the cylindrical lens slightly and observe that the spurious line from a single grain rotates with the lens, whereas the image of a spectral line ceases to remain a single solid line. The intensity of the line produced by the cylindrical lens from an object point de-

[3] Carnegie Institution of Washington Year Book No. 29, p. 178, 1929–1930.

creases toward the ends and differs in this respect from the line produced by a vibrating image. This difference accounts in part for the greater prominence of spurious lines in the image from the cylindrical lens. The cylindrical lens may also be placed in front of the objective or in the exit pupil of the microscope, but its effect is there less pronounced. Anderson found that, in an iron-arc spectrogram taken in the first order of a concave grating of one meter radius, "the precision of wave-length measurements is increased probably three-fold by the use of the cylindrical lens. Without the lens, doublets whose separation on the plate is less than 0.02 mm cannot be resolved. With the cylindrical lens several rather strongly exposed pairs with separations of 0.008 and 0.010 mm are easily divided, and moderately exposed doublets separated by 0.006 to 0.008 mm are resolved, thus indicating that the limit of resolution in the region λ2700 to λ3000 may be about 0.005 mm. The theoretical limit in the same spectral region for this grating, assumed to be a perfect optical instrument, is 0.0045 mm. Very faint lines are much easier to see and to measure with the aid of the cylindrical lens."

(c) *Tilted glass plate.* If the paths of the rays from an object point to the objective are disturbed unsymmetrically, as, for example, by the insertion of a glass plate with good optical surfaces and so inclined that the axis of the optical system, the plate normal, and the spectral line are in the same plane, the plate grains are elongated to short lines in the image with the result that the spectral lines are fused (Fig. 2D). By the use of two plates, one above the other and inclined at equal but opposite angles, the displacement of the image which results, when only a single plate is used, can be avoided. The length of the image line from an object point increases with the angle of tilt of the plates. The surfaces of the glass plate should be of fair optical quality in order not to introduce defects in the image.

(d) *Minification-magnification method.* Experience teaches that, in a microscope or telescope, two image points appear as separate, distinct points so long as the first diffraction ring or zone of the first point does not extend into the diffraction pattern of the second point beyond its central disk. If the numerical aperture of the objective is so small that only the central element of the diffraction pattern of each object point is transmitted, the result is a uniformly illuminated field incapable of producing details in the image plane. If in an object the separation of the details is less than the smallest distance that can be resolved by the microscope objective, the details cannot be seen through it no matter how highly the image is magnified by the eyepiece. Similarly if a mini-

fied image of an object is formed and the distance between two given points in the image is less than the least resolvable distance for the given objective, these two points cannot be distinguished as separate points by the microscope equipped with the given objective. A long series of tests was made to determine the validity of this conclusion that follows directly from the theory of diffraction. The minification-magnification tests proved the validity of the diffraction formula when applied to this case of the image of an image. They proved also that as the minification is increased and the image is made smaller, resolution for successively larger distances breaks down.

On a photographic negative the distribution of silver grains (clumps of silver particles) both in respect to size and to separation is not uniform. In the denser parts of the negative the silver grains are close together with but short distances between them. In the lighter parts of the negative the grains are less abundant and are more widely separated. In high speed plates the silver clumps average larger in size than in slow speed plates. Moreover the degree of uniformity in size of plate grains varies widely in plates from different manufacturers.

Applying the method of minification-magnification to plate graininess we find that a relatively low minification suffices to blend the dense areas in a photographic plate. In the case of spectral lines the fusion of grains along the line is accomplished with a much less degree of minification than is needed to fuse the grains of the background; also fusion in the dense heavy spectral lines is complete before that of the fainter lines. In practical work it is advisable to minify the image to the point at which the faint spectral lines are fused, but not necessarily the grains of the lighter background. In stellar photographs the grains are clustered about each star image with the result that on minification resolution fails first at the brighter stars and proceeds progressively to fainter stars, as the minification increases or the numerical aperture of the objective is decreased.

This method for reducing the effects of plate graininess is based essentially on the ability of the observer to decrease the resolving power of the observing optical system. This can be accomplished either by a combination of minification and magnification or by reducing the numerical aperture of the objective of the microscope. For a given case one method may be better than another; thus in the study of spectral lines the plate graininess in the lines should be eliminated, while plate graininess in the adjacent background is not serious.

(1) *Slit diaphragm.* A simple method for eliminating grain in spectral

lines is the use of a slit diaphragm in the upper focal plane of the microscope objective or in the exit pupil above the eyepiece. In this arrangement the full numerical aperture of the objective is used in the direction normal to the spectral lines, so that they are not widened; while along the lines the resolving power is so much reduced that the lines appear as solid lines and not as rows of plate grains. Each grain in the field is elongated to a short line whose length varies inversely with the width

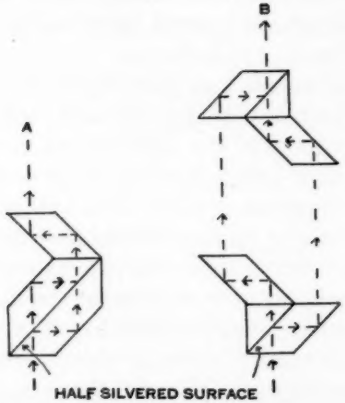

FIG. 4. *Sections of two different prism arrangements for obtaining two superposed but slightly displaced spectral image lines.*

of the slit diaphragm (Figs. 2E, 2F). By varying the slit width any degree of fusion can be obtained. For most negatives the single slit diaphragm above the microscope objective suffices. The slit diaphragm reduces the intensity of field illumination; this is an unfavorable feature, especially if a very narrow slit be used.[4]

(e) *Wollaston prism method.* On passage through a Wollaston prism an incident beam of light is separated into two slightly divergent beams of plane-polarized light vibrating in mutually perpendicular planes. A Wollaston prism plate, placed above a negative, forms two images of each plate grain; the number of grains along a spectral line is thus doubled, thereby enhancing its continuity and transforming it practically into a solid line (Fig. 2G). In practice this simple method has proved

[4] Recently Dr. J. A. Anderson of Mt. Wilson Observatory has substituted for the single slit a multiple slit, such as a half-tone screen ruled in one direction only. He thereby increases the intensity of illumination over the single slit method and obtains a degree of fusion that is satisfactory in many cases. The ruled grating may also be inserted either directly below the objective or in the plane of the exit pupil above the eyepiece.

satisfactory and useful, especially for the observation of faint spectral lines. The plane of superposition should be exactly parallel with the spectral lines. By the use of the prism arrangement of Fig. 4A or 4B above the objective a second duplication of the lines might be attained, thus increasing the number of grains along a given line four-fold. This added complication is, however, unnecessary in most cases.

(f) *Dark ground illumination.* Still another method for enhancing the distinctness of spectral lines is the use of dark ground illumination familiar to microscopists. In this method the plate is illuminated by a wide-angle, annular ring of light whose inside aperture is slightly greater than that of the microscope objective. Under this illumination each plate grain appears as an illuminated point; a spectral line appears as an illuminated line on a dark ground and not as a dark line on a light ground (Fig. 2H). This kind of illumination is readily obtained by using a condenser system of larger numerical aperture than that of the objective and stopping out the central portion of the cone of light incident upon the plate by means of a central circular stop. The spectral lines thus obtained are fused into fine luminous lines by means of any one of the foregoing methods. In many cases a more accurate setting can be made on a spectral line as it appears under dark ground illumination than under direct illumination. The examination may be made either in ordinary light or in polarized light.

Interference fringes. On many spectral lines the accuracy of setting can be somewhat increased if a strong source of light, such as pointolite or concentrated filament electric lamp at a distance, or a parallel beam is used to illuminate the plate, and the image of the line is observed slightly above or below the position of sharp focus. Under these conditions the diffraction pattern of the line consists of two or more interference fringes arranged symmetrically to the position of the line image. The use of a slit diaphragm or a cylindrical lens above the objective to fuse the spectral line increases the uniformity and distinctness of the interference-diffraction fringes.

A comparison of these different methods shows that in each case an essential factor is the quality of field illumination. If this be too strong or too weak the slight differences in contrast between a weak spectral line and the field cannot be recognized by the eye. If the angular aperture of the illuminating system is in excess of that of the objective, the field is likely to be flooded with light and this diffused glare means decrease in contrast and reduced visibility for the weak lines.

In this connection projection methods are useful in increasing con-

trast; the diffuse and scattered light is thereby eliminated to a large extent. A spectrogram, projected on a white diffusing surface, such as a magnesia-coated plate, and viewed by reflected light, or projected on a thin opal glass surface and viewed by transmitted light, shows the lines under enhanced contrast, especially if in front of the projection lens a weak cylindrical lens (0.25 diopter) or a tilted glass plate combination be placed. Weak lines are thereby rendered visible and other lines are resolved that are not resolved under ordinary conditions of observation.

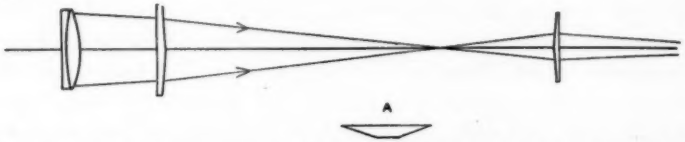

FIG. 5. *Fresnel prism arrangement for obtaining two sharp dividing lines between two sets of adjoining spectral lines. Fig. 5A. Truncated Fresnel prism arrangement for obtaining two sharp dividing lines between a central set of spectral lines and two outer sets of comparison spectral lines.*

On a spectral line that is properly fused to a thin continuous line a more accurate position measurement can be made if the reference or fiducial line of the measuring instrument does not cover the entire length of the line. A more exact setting can be made on two lines that abut end to end than on two superposed lines. On many spectrograms, a series of standard spectral lines from a known source of light is photographed to serve as reference lines in the measurement of the spectral lines emanating from the object under investigation. Such measurements can be most accurately made when the two or three sets of lines abut end to end as in a range-finder field. There are several optical arrangements for attaining this object. In Fig. 5 two roof-shaped or Fresnel prisms are shown placed between objective and eyepiece. The prism nearest the objective can be shifted along the axis, while the second prism is placed with its roof edge in the image plane of the eyepiece. This arrangement gives a sharp dividing line, like that of a photometric field, and places the two series of spectral lines in juxtaposition. On moving the objective prism toward the objective the two images tend to separate[5] and vice versa. If the roof edge on each prism is truncated by a face parallel with the base, Fig. 5A, a central and two outer sets of spectral lines can be viewed in the field; each outer set is separated by a sharp line from the central set.

[5] A detailed description of this arrangement is given in F. E. Wright, *A polarization photometer eyepiece.* J.O.S.A. & R.S.I., *14*, 339–341, 1927.

The elimination of plate graininess in spectral lines that are to be placed in juxtaposition is not easily accomplished by use of the cylindrical lens so placed that it extends each object point into a relatively long line, or of a Wollaston prism which produces overlapping images. Other methods, such as that of the vibrating image, or of the tilted plates, or of minification-magnification, are, however, applicable.

A comparison, with reference to the intensity of illumination of the image, of the methods for spectral line fusion shows that the Linnik method gives the brightest image. The vibrating glass plate or lens, the cylindrical lens method of Anderson, the Wollaston prism method, and the tilted glass plate method yield images 8 to 10 percent less bright. The minification-magnification method produces an image 25 to 75 percent as bright; while the single slit diaphragm, depending on its width, transmits from 1/2 to 3 percent of the light entering the objective. The multiple slit or grating method of Anderson transmits correspondingly more light, up to 40 percent. With dark ground illumination the intensity of illumination of the field depends on a number of factors, such as the excess numerical aperture of the condenser over that of the objective, and the character of the object illuminated. This method is not directly comparable with the foregoing methods because of the different character of its field.

STELLAR IMAGES

There are relatively few methods available for reducing the effects of plate grain in star images. The method of the vibrating image that is successful with spectral lines might be replaced by that of an irregularly oscillating image, but, as a practical basis for accurate measurements, this method is not promising. The only feasible plan seems to be to reduce the resolving power of the observing system either by the minification-magnification method or by the use of an iris diaphragm in the rear focal plane of the objective. In either case the resolving power should be cut down only to the point for which the plate grains affecting the given star under measurement are fused. To reduce the resolving power below this limit cuts down the illumination and broadens the diffraction patterns of the stellar images. In certain cases dark ground illumination is useful, but commonly the direct image is preferable, because of the better illumination.

The method of minification-magnification can be applied to several other problems, such as the measurement of the average separation of the grains in a photographic plate, also to the reduction of the promi-

nence of the dots in half-tone illustrations. To ascertain the average separation of the grains in a photographic plate, determine the degree of minification needed to produce a fairly uniformly illuminated field. In this case the average distance between the individual grains that have been fused is measured; this in itself is an indication of the average degree of packing of the grains. The measurement does not give a measure of the average plate grain size in the usual sense.

If a minified image of a half-tone illustration is produced by an objective of low numerical aperture the dark portions of the illustration blend and become solid; with further minification the half-tone lattice work disappears over the greater part of the illustration. If it is desired to reproduce a half-tone, a more natural reproduction can be obtained by the minification-magnification method than by a direct photograph.

In all these observations and measurements it is important that the intensity level of the illuminated field be suited to the objects under observation; also that the aperture of the illuminating system be adapted to that of the imaging system, otherwise glare is introduced and the contrast is decreased. It is well to employ a source of light whose intensity and aperture can be varied at will in order to obtain the optimum conditions for observation.

In the minification-magnification method the degree of minification depends on the degree of separation of the plate grain and on the special details of the negative for which the grain is to be eliminated. In each case that degree of minification only should be employed which accomplishes the desired result. To minify in excess of this limit serves no purpose and imposes difficulties on the magnifying part of the observing system.

THE WAVE-LENGTH-SENSITIVITY CURVE OF A CESIUM OXIDE PHOTOCELL; A NEW LIGHT-SENSITIVE INSTRUMENT FOR THE ULTRAVIOLET

By T. F. Young and W. C. Pierce

[George Herbert Jones Laboratory of the University of Chicago and the G-M Laboratories, Inc., Chicago, Illinois.]

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ABSTRACT

The construction and characteristics of a quartz-enclosed cesium oxide cell are described. Such a cell is very sensitive to ultraviolet light of very short wave lengths, at least as short as 2390A.

The commercial importance of cells of the cesium oxide type is due largely to their high sensitivity to red and infrared light. Recently Ballard[1] has demonstrated response to light of wave length longer than

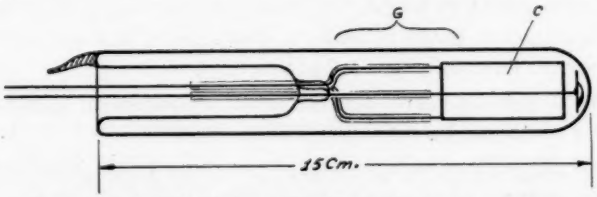

Fig. 1. *Quartz-enclosed photoelectric cell. C, cathode; G, graded seal.*

10,000A. According to his results and the original work of Koller,[2] a glass-enclosed cell is sensitive to light of wave lengths between about 2900A and 12,000A. There are two maxima in the wave-length-sensitivity curve, one at about 3500A and the other in the neighborhood of 7500A.

For the study of the response of a cesium oxide surface to light of wave-lengths shorter than 3000A, a quartz-enclosed cell was designed and constructed by G-M Laboratories, Inc. In Fig. 1, *G* represents a quartz-pyrex graded seal. The cathode and anode are supported on tungsten wires which also serve as electrical conductors. Each wire is surrounded by a long Pyrex tube to reduce electrical leakage. The cathode, *C*, is a silver-plated copper sheet coated with a thin photosensitive layer. Production of sensitive cesium-oxide-silver layers has been described by Koller.[3] Methods have also been discussed by Davies

[1] Ballard, J.O.S.A., *20*, 618; 1930

[2] Koller, J.O.S.A. & R.S.I., *19*, 135; 1929.

[3] Koller, J.O.S.A. & R.S.I., *19*, 135; 1929; Phys. Rev., *36*, 1639; 1930.

and Ruff[4] and by Zworykin and Wilson.[5] The cell used in this work contained argon.

APPARATUS

1. Light was supplied by a water-cooled mercury lamp operating at a pressure of one atmosphere. It was a modification of the constricted arc lamp described by Forbes and Harrison.[6] About 2.5 amperes maintained the discharge in a quartz capillary of about 0.2 centimeter internal diameter.

2. The monochromator was a constant-deviation instrument built by Bausch and Lomb. It contained two thin quartz prisms which could be rotated simultaneously in opposite directions by means of a "wavelength screw." Another screw moved each of the two thin aspheric lenses to a distance from its corresponding slit, equal to its focal length. All three screws were equipped with drums calibrated directly in wave lengths from 2000A to 8000A. Near the exit slit was a slide provided with a fluorescent uranium glass, a clear space, and an intervening opaque space. This slide was used as a shutter.

3. The thermopile was an eighteen junction instrument manufactured by Kipp and Zonen. Its resistance was 31 ohms.

4. Two galvanometers were used. One was a Leeds and Northrup, Type HS instrument of about sixteen ohms resistance. It was nearly critically damped by the thermopile. The other, used with the photoelectric cell, was a Type R galvanometer of the same make. It was damped by a resistance of about 10,000 ohms connected across its terminals. An Ayrton shunt was employed in conjunction with this instrument.

A potentiometer and standard resistance were used to demonstrate that the deflections of each galvanometer were proportional to the current passing through it. For a deflection of one centimeter the low and high resistance galvanometers required currents of 5.7×10^{-8} and 1.6×10^{-9} ampere respectively.

5. The experimental arrangement is shown in Fig. 2. The light source,

[4] Photo-Electric Cells and Their Applications, A Discussion at a Joint Meeting of the Physical and Optical Societies, June 4 and 5, 1930, Editor: John S. Anderson; The Physical and Optical Societies, London, 1930, page 43; Davies and Ruff, The Manufacture and Use of the Thin-Film Caesium Cell for Sound Reproduction.

[5] Zworykin and Wilson, Photocells and Their Application, John Wiley and Sons, Inc., New York, 1930, page 55.

[6] Forbes and Harrison, J.O.S.A. & R.S.I., *11*, 99; 1925.

L, was placed about 3.5 centimeters from the collimator slit. No lens was interposed. The pile, *TP*, and the cell, *PC*, were mounted on a sliding metal rack equipped with adjustable stops which limited its lateral motion. The thermopile and photoelectric cell were protected from stray light by various shields and a black cloth cover. Very little scattered light reached them.

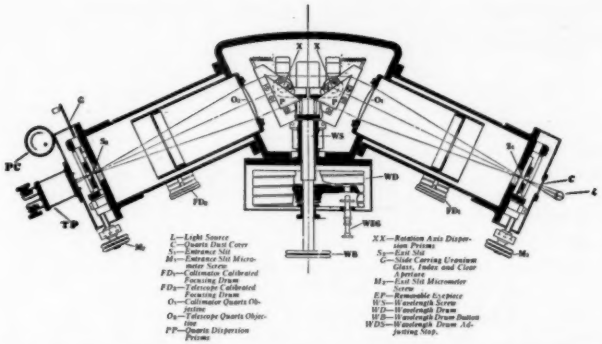

FIG. 2. *Arrangement of apparatus. TP, thermopile; PC, photocell; L, light source.* (*Diagram of monochromatic illuminator reproduced by permission of Bausch and Lomb.*)

The 0.4 centimeter slit of the thermopile was approximately as wide as the light beam but high enough to admit only about half of it. Though farther from the monochromator slit, the plate of the photoelectric cell was large enough to accomodate the whole beam.

PROCEDURE

For the determination of the wave length-sensitivity curve of the cell, the monochromator slits were opened to a width of 0.05 centimeter. The three drums of the monochromator were set for any selected wave length, usually a line of the mercury arc spectrum. The slide near the exit slit was moved to shut off the light and the rack moved against the proper stop to put the pile precisely in front of the slit. The shutter was opened, then closed and the corresponding galvanometer deflections observed. The photoelectric cell was then moved into position and similar galvanometer readings made. The table is a record of typical measurements made with 22.5 volts in the photocell circuit. The currents produced by 90 volts were 6.25 times those produced by 22.5 volts. Exposed to light of 2537A, the photocell with 90 volts in its

circuit produced deflections approximately 100 times those produced by the thermopile.[7]

It was not feasible to measure the response to light of wave length shorter than 2500A because the constricted arc used did not supply enough energy to affect the thermopile sufficiently. Because of the low dispersion of red light by quartz the accuracy is not high for light of the longer wave lengths. Very much higher precision throughout could have been attained had more detailed knowledge of the characteristics of this particular cell been of general interest.

Table of Typical Data

Wave length (Ångström units)	2537	2699	3132	3663	4078	5461
Deflection of thermopile galvanometer (centimeters)	1.25	1.1	5.8	10.3	2.65	7.8
Deflection of photocell galvanometer (centimeters)	20.5	11.9	34.8	23.0 ×10	35.9	6.5 ×10

The value of the new cell for measurement of light intensities is illustrated by the following experiment: The slit of the monochromator was narrowed to 0.01 centimeter; galvanometer deflections were determined and plotted as a function of the wave-length settings of the monochromator; they were sufficiently large to define sharp peaks at 2390, 2480, 2540, 2650, 2700, 2800, etc. Angström units.

The cesium oxide cell was compared with an efficient cell containing a sodium surface sensitized by a glow discharge in hydrogen. Between about 2750A and 3400A, the latter operating with about 135 volts in its circuit was superior to the cesium oxide cell operating with 90 volts. To light of other wave lengths the cesium cell was the more responsive.

DISCUSSION

The ratio of the galvanometer deflections at each wave length is exhibited in Fig. 3. The portion of the curve between 8000A and 12,000A was estimated with the aid of the curves of Ballard[8] who found large

[7] This corresponds to one electron in the circuit of the gas filled cell for about ten to thirty quanta. (λ=2537A).

[8] Ballard, J.O.S.A., *20*, 618; 1930

differences in the characteristics of various cells. This part of the curve is, therefore, only approximate.

More experiments must be made with light of wave lengths shorter than 2500A and in the neighborhood of 3200A. Because of the sharpness of the minimum between 2500 and 3500A this region is unusually adaptable for the study of relative amounts of light reflected and ab-

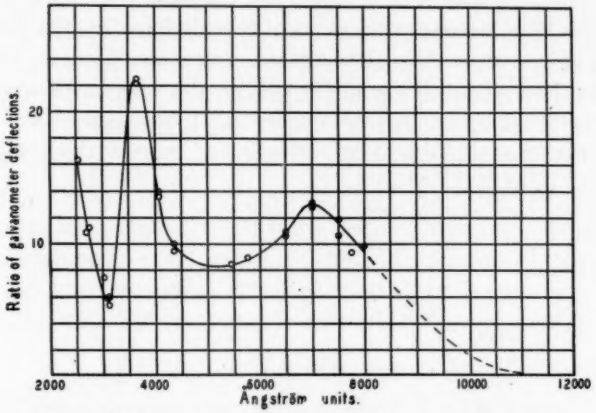

FIG. 3. *Relative response of cesium oxide photoelectric cell to light of various wave lengths.*

sorbed by a photo-sensitive surface. It may prove significant that the surface responds least to light of about that same wave length which is best transmitted by thin films of silver deposited upon glass.[9]

The relatively high response to light of wave lengths shorter than 3000A is apparent in Fig. 3. Hitherto this characteristic has been obscured by the construction of commercial photocells. To light of these very short, as well as of longer, wave lengths the quartz-enclosed cesium-oxide-silver cell is a very sensitive photometric instrument.

[9] International Critical Tables, McGraw-Hill Book Company, New York, 1929, vol. 5, p. 255.

THE ERRORS DUE TO THE FINITE SIZE OF HOLES AND SAMPLE IN INTEGRATING SPHERES

By Arthur C. Hardy and O. W. Pineo
[Massachusetts Institute of Technology
Cambridge, Mass. Received April 27, 1931]

The usual theory of the integrating sphere as used in reflectometry assumes that the sample to be tested and the holes in the sphere through which it is illuminated and viewed are of negligible size. The purpose of this paper is to show that, although the sample and holes may be small in comparison with the size of the sphere, the error in the reflectance measurements may be far from negligible. In one method of using the sphere, the error introduced by a sample and holes of the usual dimensions may be as much as 25%.

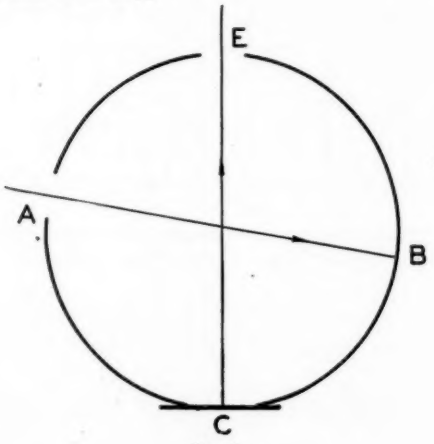

Fig. 1

Case I

This case, which represents what may be called the substitution method,[1] is represented diagramatically in Fig. 1. Light enters the sphere through aperture A and falls on the sphere wall at B. The brightness of the sample at C is measured by means of an external photometer through aperture E. The sample is then replaced by a standard and the measurement of brightness is repeated. The ratio of these two brightnesses is assumed to give the relative reflectance of the sample.

[1] This is essentially the method used by Priest in his colorimeter (J.O.S.A. and R.S.I. *8*-173; 1924 and seems to be the method employed at present in the photoelectric spectrophotometers devised by Mulder and Razek and by the American Photoelectric Corporation.

We will now calculate the error in the relative reflectance caused by the finite area of the sample and the holes at A and E. This calculation will be based on the assumption that the sphere is uniformly coated with a material obeying Lambert's cosine law.

Let A = total area of the sphere
a = area of the sample
α = area of the holes
S = the reflectance of the sphere walls at some wave length λ
r = reflectance of the sample at the same wave length λ
R = reflectance of the standard at the same wave length λ
F = the amount of flux of wave length λ entering the sphere.

The flux F that enters the hole A strikes the sphere wall at B. Some of this flux is absorbed, but an amount FS is diffusely reflected. The reflected flux either escapes through the holes at A and E or is absorbed by the sample or the wall of the sphere. The amount of flux escaping through the holes is $i\alpha$, where i is the uniform illumination at any point of the sphere wall. The amount of flux absorbed by the sample is

$$i(1 - r)a.$$

Similarly, the amount absorbed on the walls of the sphere is

$$i(1 - S)(A - a - \alpha).$$

Equating the amount of flux diffused into the sphere to the amount that escapes or is absorbed, we have that

$$FS = i[\alpha + (1 - r)a + (1 - S)(A - a - \alpha)]. \tag{1}$$

Now, when the sample is replaced by the standard, unless the reflectance of the standard is the same as that of the sample, the illumination on the walls of the sphere will be different. Let the new value of the illumination be I. Again equating the flux diffused into the sphere to that which escapes or is absorbed, we have that

$$FS = I[\alpha + (1 - R)a + (1 - S)(A - a - \alpha)]. \tag{2}$$

Let b be the observed brightness of the sample and B that of the standard. Since, in the proper units,

$$b = ri$$

and

$$B = RI$$

it follows that

$$\frac{r}{R} = \frac{b}{B} \cdot \frac{I}{i} . \tag{3}$$

The ratio I/i is easily found from equations (1) and (2) to be

$$\frac{I}{i} = \frac{A - S(A - a - \alpha) - ar}{A - S(A - a - \alpha) - aR} = 1 + \frac{a(R - r)}{A - S(A - a - \alpha) - aR} . \tag{4}$$

Since, according to the simple theory of the sphere,

$$\frac{r}{R} = \frac{b}{B},$$

the quantity I/i may be regarded as a sort of correction term which takes account of the effect of the sample and holes. Ordinarily, the area of the sample is approximately 1% of the total sphere area and the holes usually account for a similar fraction. If the sphere is coated with magnesium oxide ($S = 0.97$), the correction factor

$$I/i = 1 + 0.252(R - r). \tag{5}$$

When a black sample ($r = 0$) is compared against a magnesium carbonate standard ($R = 0.98$), the illumination on the standard is 25% greater than that on the sample, so the correction factor is 1.25. The error disappears, of course, when the reflectance of the sample is the same as that of the standard, but, even for samples reflecting as much as 50%, the error is 12%. Usually R and S are substantially neutral and of high reflectance, but r varies with the wave length. If the sphere is used in a colorimeter, the greater error at low values of reflectance results also in an increase in the apparent saturation of the color.

The sphere sketched in Fig. 1 was taken merely as an illustration of the substitution method, which is characterized by the principle that the sample and standard occupy successively the same position in the sphere wall. Many variations of this method are possible but they all lead to substantially the same error. Even placing lamps inside the sphere and screening the sample from their direct radiation can be shown to result in an error given by

$$\frac{I}{i} = 1 + (R - r)\left[\frac{a}{A - S(A - a - \alpha) - aR} - \frac{a}{A}\right]$$

which differs only slightly from that given by equation (4). For the numerical case considered, the factor is

$$1 + 0.242(R - r) \text{ instead of } 1 + 0.252(R - r).$$

Of course, the presence of the lamps within the sphere may lower the average reflectance of the sphere wall and indirectly reduce the error somewhat.

CASE II.

Case II is characterized by the principle that the brightnesses of the sample and standard are compared simultaneously, instead of succes-

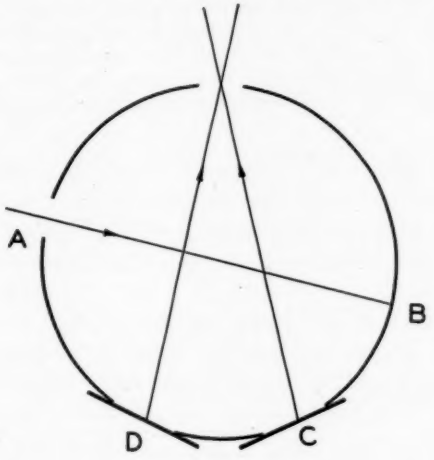

FIG. 2

sively as in Case I. A schematic representation of such a sphere is shown in Fig. 2. Light enters the hole *A* and falls on the sphere wall at *B*. The sample at *C* and the standard at *D* are both a part of the sphere wall at all times. In a properly designed sphere, they receive equal illumination and the relative brightness of the sample and standard is, therefore, a true measure of the relative reflectance.

Although this method does not suffer from an error of the sort discussed in Case I, it is nevertheless desirable that the sample and standard should be small because they are usually plane, instead of spherical as required by the theory of the sphere. If the sample is spherical, the illumination at any point of the sample is due in part to flux coming from other parts of the sample, whereas if the sample is plane, the illumination is due entirely to flux coming from the sphere wall. Since the reflectance of the sample is usually less than that of the sphere wall, the

illumination is greater in the case of a plane sample. The correction factor to be applied when a plane sample is used is given approximately by:

$$1 - \frac{a(1 - r)}{A}.$$

For the numerical cases considered above, the error is, for most samples of the order of 1%.

THE COLOR AND INTENSITY OF THE CHEMI-LUMINESCENCE OF SOLID SODIUM

By Robert M. Bowie

[Physics Department, Iowa State College, Ames, Iowa.

Received April 6, 1931]

ABSTRACT

The fact that solid sodium reacts with the moisture in the air to produce a faint glow has been known for years. The color of the light was said to be greenish and its intensity extremely low, although no careful measurements had been made. In this article a method is described for determining its intensity by means of a photoelectric cell. The determination of the spectrum of the light as obtained both by filters and spectrographically is also described. The intensity was found to vary from 3.5 to 10.5×10^{-7} lumens per square inch of sodium surface while the spectrum was found to consist of a band between 5000A and 5300A with a maximum at about 5100A.

Sodium is a soft metal with a silvery luster when the metal itself can be seen. However a freshly cut surface tarnishes in a fraction of a second when in contact with air. Even as long ago as the time of Davy[1] it was known that this tarnishing process produced a faint greenish light when viewed in the dark.

Linnemann[2], in 1885, stated that freshly cut surfaces of sodium and potassium exposed to air in the dark become phosphorescent. The sodium exceeded the potassium in brightness, giving a greenish glow while the latter produced a reddish glow. At about 60°C or 70° sodium glowed as brightly as phosphorus.

G. Rebaul[1] carried out a more comprehensive study of the effect, the results of which were published in 1910. One may judge from his statement that he found the luminescence to be very weak, as he describes the phenomenon as follows:

"The luminescence may be distinctly perceived only after staying in the dark about 15 minutes. At times it is advantageous to use photographic plates which are impressioned at the end of two or three minutes. The impression is very distinct after about 10 minutes of exposure and suffices then for a study of the phenomenon."

In the determination of the intensity of the light it was thought best not to employ a method requiring a visual comparison inasmuch as the intensity of the light was so exceedingly low. Therefore a vacuum type caesium photoelectric cell was used, the current through which was measured by means of a Compton electrometer.

[1] G. Rebaul, *Compt. rend. 168*, 1195; 1910.

[2] E. Linnemann, *J. f. Prak. Chem. 75*, 128; 1858.

The cell was designed for a small dark current as the cathode connection was located at the rear of the tube. The anode connection was made through one prong in the base. The cell was very carefully shielded from both external light and electrostatic effects. The only insulation on the lead from the cathode of the tube was the amber supporting the quadrants of the electrometer and the glass of the tube. But even with this

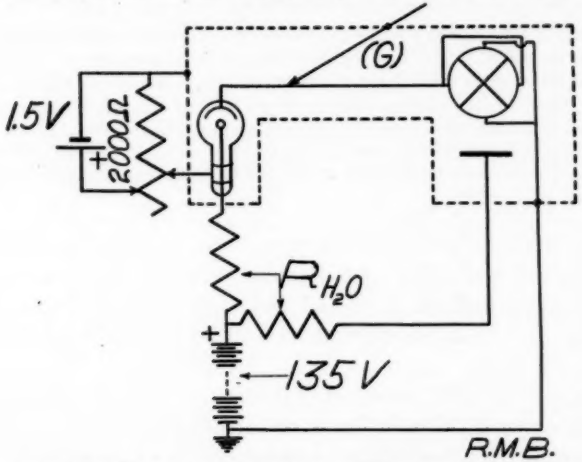

FIG. 1. *The color and intensity of the chemiluminescence of solid sodium.*

arrangement there was a marked dark current. To eliminate this it was not only found necessary to place a metallic collar about the neck of the cell but to place it at a potential slightly below ground by means of a potentiometer arrangement. The complete circuit is shown in Fig. 1.

The collar consisted of an iron ring, which fitted about the base of the tube, surrounded by a large rubber tube. The space between the neck of the cell and the iron collar was filled with mercury. With this collar placed at a potential of about 0.6 volts below ground the earthing contact *G* could be broken and the electrometer indicator would remain within one mm of zero for fifteen minutes at a time.

With light falling on the cell the deflection of the indicator did not increase constantly at a rate proportional to the light intensity, but came to a constant reading on the scale as though there were in parallel with it a very high resistance. This was due to the leakage over the glass.

In determining the intensity of the luminescence a circular slab of sodium metal 1.75 inches in diameter was thrust up the tube to within 0.9 inch of the photoelectric cell. A glass window and a grounded screen

were placed between the sodium and the cell. Before thrusting the metal into the tube, its surface was first renewed by breathing upon it. This caused it to glow quite brightly. At intervals the reaction product was cut away to produce a new surface of sodium. This is indicated in Table 1 by the statement, "New Surface." The maximum deflections of the electrometer are also given in the table.

TABLE 1. *The intensity of the chemiluminescence of solid sodium.*

Number of observation	Deflection (cm)	Luminescence (lumens/in^2)
New surface	just taken from kerosene	
(1)	4.2	
(2)	5.5	
(3)	4.1	
(4)	4.0	
Ave.	4.4	3.57×10^{-7}
New surface	Na getting warm	
(1)	7.0	
(2)	6.7	
Ave.	6.9	5.6×10^{-7}
New surface	Na warm, (40 to 50°C)	
(1)	10.4	
(2)	14.3	
(3)	14.1	
Ave.	12.9	10.5×10^{-7}
New surface	after cooling in kerosene	
(1)	4.4	3.75×10^{-7}
New surface		
(1)	8.8	
(2)	8.0	
Ave.	8.4	6.8×10^{-7}

Inasmuch as it is quite possible that thrusting a metal surface to within such a short distance of the cell might cause a change in capacity of the system which would cause a deflection of the instrument, a check was made in which no light was produced. The slab of sodium, having never been cut on the back side, was coated with a layer of NaOH which emitted no light. When this surface was thrust in to the same position the deflections given in Table No. 2 were obtained. Evidently the electrostatic shielding was sufficient.

This piece of luminescent sodium was closer than its own diameter to the window of the photoelectric cell. For this reason it could not be considered as a point source so that the inverse square law could not be used. Therefore an approximation was carried out to determine what percent

of all the light given off by every point on the surface in every direction entered the cell window. This value was found to be 40.6 percent.

Since a caesium photoelectric cell had a maximum sensitivity at about 5300A and the maximum intensity for the emitted light, as will be shown later, was about 5100A, nearly all the emitted light was effective on the cell. In calibration, therefore, it was also necessary to use a light giving a maximum in that vicinity. To do this a Wratten 44a filter

TABLE 2. *Dark shift of electrometer due to change in capacity when metal was inserted.*

Number of observation	Deflection (cm)
Right after first run listed in Table No. 1.	
(1)	0.4
(2)	0.2
Ave.	0.3
Right after second run listed above.	
(1)	1.8
Right after fourth run listed above.	
(1)	0.5

was used with a mazda C lamp. Knowing the sensitivity of the instrument and the percent of light from the metal which entered the cell, the values of intensity given in Table 1 were computed.

The reason for the constantly increasing intensity throughout the first three sets of readings and again through the last two, was probably the gradual increase in the temperature of the metal.

The spectrum of this luminescence was difficult to obtain due to the weakness of the source. Early experiments with ordinary photometers revealed a lack of light gathering power sufficient for the purpose. For this reason, use of a set of filters was resorted to. The set consisted of 24 selected Wratten filters the most important of which are listed by number in Table 3. Along with the numbers are also given the percentages of light passed by each at 5000A and 5300A. These values were taken from the tables.[3]

In the experiment a large surface of sodium was caused to glow by cutting away the reacted surface and breathing upon the fresh metal. In this condition a filter was placed partly over the surface and an estimate of the percentage of the light passed was made. The averages of a number of such estimates are recorded in columns 2 of Table 3.

From these data and the tables[3] mentioned above, the location of the luminescence was found to lie between 5000A and 5300A with a max-

[3] Wratten Light Filters sixth edition, revised, Eastman Kodak Company, Rochester, New York. 1924.

TABLE 3

Filter no.	Percent passed	Percent transmitted by filter at[4] 5000A	5300A
8	90	58.8	74.9
9	75	33.3	68.9
12	60	2.5	64.0
15	60	0	57.0
22	10	0	0
23	0	0	0
29	0	0	0
30	40	13.8	0
35	0	0	0
44a	45	41.8	22.9
45	35	34.9	8.0
49	5	0.5	0
50	0	0	0
58	50	30.3	54.7
60	70	49.0	55.2
61	50	17.8	33.8

imum at about 5100A. These results are subject to an error of about 100A due to the weakness of the source.

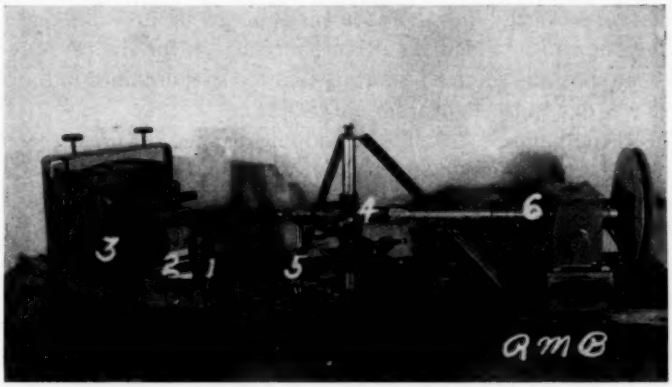

FIG. 2. *The color and intensity of the chemiluminescence of solid sodium.*

As has been mentioned before, the light gathering power of an ordinary spectrograph is too low for use in this experiment. For this investigation, therefore, a special instrument was made at the College Instrument Shop. The spectrograph proper is to be seen at the left end of Fig. 2. The collimator lens at (1) is an f 4.5, 5½ in., Kodak Anastig-

[4] These values are taken from Wratten Light Filters, *ibid.*

mat lens. The parallel rays of light from it then passed through the large, 60°, crown glass prism shown at (2). The spectrum thus produced was focused on an Eastman 40 plate by the f 4.5, $5\frac{3}{4}$ in., Cooke Anastigmat lens in the Thornton Pickard camera shown at (3).

On account of the very low intensity of the light, no slit was used. In its place a thin sodium wire was exuded slowly through a No. 70 drill hole in the nozzle of a mechanically operated pressure gun. In Fig 2 the pressure gun is shown at (4). Its nozzle is shown at (5). The pressure was produced by turning a threaded rod inclosed in the slotted sleeve. This sleeve was turned at the rate of one revolution in 15 minutes by the reduction gear and motor located at (6). The wire thus produced formed a thin, straight, luminescent source located vertically in the focal plane of the collimator lens. Exposures of from six to eight hours were used. This was the maximum time during which sodium could be exuded before filling the pressure gun. During all runs a stream of air was passed over the freshly exuded wire to keep it luminescent.

The resulting spectrograph consisted of a faint spot, which when compared with the mercury arc spectrum, was found to be a general radiation with a maximum somewhere about 5100A. Its extent was hard to estimate. Identically the same spot was obtained in three different runs. During one run in which the driving mechanism for the pressure gun broke, no spot was obtained, showing that the spot obtained in the other plates was due to the light from the sodium.

The chemiluminescence of solid sodium in open air was, therefore, found to be of the order of intensity of 3.5 to 10.5×10^{-7} lumens per square inch of sodium surface. The intensity evidently increases with the temperature. Use of filters indicated that the luminescence was a general radiation lying between 5000A and 5300A with a maximum at about 5100A. The error involved was probably of the order of 100A. By spectrographic means, also, the luminescence was found to be a general radiation with a maximum at about 5100A.

The author is deeply indebted to the Physics Department of Iowa State College for the loan of the apparatus and for the materials used in this investigation. He also wishes to thank Dr. G. W. Fox for the use of his photoelectric cell and for his interest and helpful suggestions. Particularly, he wishes to thank Dr. J. W. Woodrow, under whose guidance this work was carried to completion.

A FURTHER STUDY OF GALVANO-LUMINESCENCE

By Roy Richard Sullivan and R. T. Dufford

[Department of Physics, University of Missouri, Columbia, Mo. Received March 9, 1931]

This paper reports a study which is a continuation of earlier work by one of the writers.[1] In the earlier article in this journal, the brightness and the efficiency of the luminescence occurring at aluminum and other anodes, in solutions of a number of compounds, were studied and plotted as functions of the applied voltage; it was shown that each increases very rapidly with the voltage up to a certain point, beyond which each decreases, owing to overheating and consequent destruction of the film on the electrode. It was suggested that higher efficiencies might be obtained by using water-cooled electrodes. The present work makes a study of the extent to which the brightness and efficiency can be increased by cooling the electrodes, and extends the study to new solutions. Also, a systematic study of the behavior of various metals in ether solutions of Grignard reagents is included.

The case of aluminum anodes in aqueous solutions will be taken up first. This glow seems to have been noticed first by Lemon,[2] who noted the increased brightness when the voltage was increased. Such a glow on lead electrodes in sulphuric acid was pointed out much earlier by Schluederberg;[3] and similar glows on the surfaces of anodes of mercury, tin, copper, cadmium, silver, and lead, were described by Bancroft and Weiser,[4] who, after careful study, came to the conclusion that the glow is due to the rapid reaction of the nascent halogens (or other electrolytic products) with the anode metals, within a film made up of the solid salt resulting from the reaction. They decided against a theory of luminescence of the film itself, and against the existence of a gas film. The effect with mercury anodes has been discovered independently by Dumanski,[5] at Woronesh, U.S.S.R. In a recent article, Harvey[6] has described two additional cases of the phenomenon, and has suggested for it the name galvano-luminescence, which seems well worth adopting. Harvey

[1] Dufford, R. T., J.O.S.A. and R.S.I. *18*, 17; 1929; Dufford, Nightingale and Gaddum, J. Am. Chem. Soc. *49*, 1858; 1927.

[2] Lemon, Harvey B., Science, *47*, 170; 1918.

[3] Schluederberg, H., J. Phys. Chem. *12*, 623; 1908.

[4] Bancroft, W. D., and Weiser, H. B., J. Phys. Chem. *18*, 762; 1914.

[5] Dumanski, A., Ceschewa, A., and Banow, A., Zts. f. phys. Chem. (B) *3*, 440; 1929.

[6] Harvey, E. Newton, J. Phys. Chem. *33*, 1456; 1929.

also suggests a mechanism, essentially an oxidation by hydrogen peroxide, for the production of the light in the cases he describes.

The effect with aluminum electrodes, as with tantalum and, to a less extent, with tungsten, is associated with a marked degree of mechanical passivity; the films formed on the metal show pronounced unilateral conduction. Commercial application has been made of the properties of the films, in two directions: to electrolytic rectifiers,[7] and to electrolytic condensers,[8,9] the thin film separating the electrode from the solution giving rise to very high capacitance per unit area. Güntherschulze[7] and others have suggested that a layer of oxygen gas must exist between the metal and the oxide film which covers it, and that this gas layer is the effective part of the film in the rectification process. Other workers[10] have advanced other theories which they believe better suited to explain the rectifying action. In a recent article, which appeared some months after the present work was finished, Forrest[11] has studied the glow around anodes of aluminum, tantalum, and tungsten; while accepting the theory of the film of oxygen, he shows that the evidence is not entirely in accordance with that hypothesis. Additional evidence which also seems contrary to the gas film hypothesis will be pointed out below.

The measurements in the present investigation were made with apparatus quite similar to that used in the preliminary investigation[1] at Nela Park. A precisely similar photometer was used, with the same calibrated bulb, for which the relative candlepower was known as a function of the voltage. The apparatus was rebuilt. but to the same dimensions, and was recalibrated against brightness standards calibrated by the Bureau of Standards. The final calibration curve was closely similar to the older curve used in the earlier work. In computing luminous efficiencies, the value 620 lumens per watt was used for the mechanical equivalent of light.

Studies on phosphate solutions indicated that the earlier results were reproducible within the limits to be expected; curves quite similar to those previously published were obtained. A study was made to see how the brightness of the glow varies with time, at various voltages; the glow does not become steady in brightness for about ten minutes after the

[7] Güntherschulze, A., *Electric Rectifiers and Valves*, transl. by N. A. deBruyne (1928).
[8] Siegmund, H. O., Bell System Tech. Jour. *8*, 41; 1929.
[9] Maddison, R. E. W., Phil. Mag. *8*, 29; 1929.
[10] Pietenpol, W. B. and Friesen, A. B., Phys. Rev. *33*, 277; 1929.
[11] Forrest, J. S., Phil. Mag. *10*, 1003; 1930.

voltage is applied, but it changes relatively little after that. The total variation with time, however, is much less than the variation with applied voltage shown in the curves, so that, while readings taken a short time after the voltage is applied will be larger than later readings, the general trend of the curves so obtained will not be changed. The de-

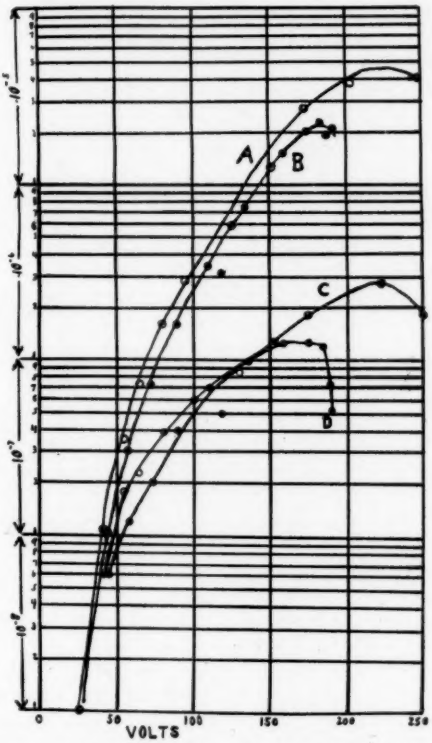

FIG. 1. *Effect of water-cooling aluminum anode in tri-sodium phosphate solution. A and B are the brightness curves for the glow (the ordinates are lamberts), C and D the efficiency curves (the ordinates are percentages). The data for the water-cooled electrode are indicated by circles.*

crease in brightness appears to be due partly to the decrease in the current as the film increases in thickness, and partly to the fact that the thicker film absorbs more of the light. The decrease appears to continue until no further increase in the thickness of the film occurs. A scratch made in the film will be brighter than the surrounding area for several minutes, until the film over the scratch attains the same thickness as the adjacent film.

By using a cylindrical aluminum anode cooled with circulating tap-water, it was found that readings could usually be carried to considerably higher voltages before the heat developed at so rapid a rate as to break down the film. And, as suggested in the previous article, at these higher voltages, the brightness and the efficiency become larger than without the water-cooling. The curves shown in Fig. 1, which illustrate a typical run with a tri-sodium phosphate (Na_3PO_4) solution, are fairly

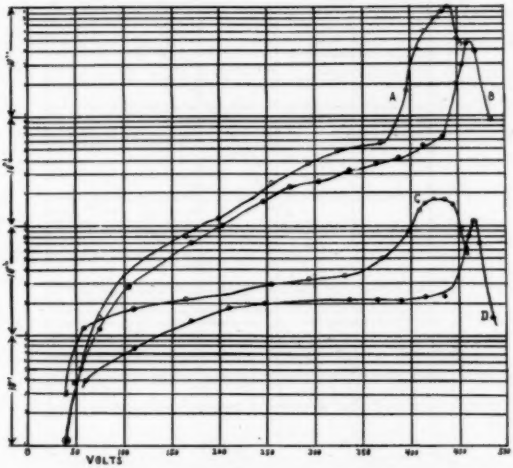

FIG. 2. *Effect of water-cooling aluminum anode in ammonium borate solution. A and B are the brightness curves (ordinates are lamberts), C and D are the efficiency curves (percentages). The marked rise at the upper ends of these curves occurs when the effect of the scintillations which appear at high voltage is added to that of the glow.*

characteristic of the results obtained with all the phosphate solutions except the pyrophosphate; i.e. from sodium phosphite, mono-sodium phosphate, di-sodium phosphate, and tri-sodium phosphate. In these solutions, the increase in the efficiency is much more pronounced than the increase in the brightness. It is a notable fact that with these solutions the light comes chiefly from the steady glow, with very little being contributed by the scintillations which sometimes appear on the electrodes.

It seemed of interest to extend the investigation to ammonium borate solution, since this is the substance most frequently used in electrolytic condensers, and since it had not previously been tested in the investigation of luminescence. For comparison, sodium borate solution was also tested more thoroughly than before. These substances are dif-

ferent in behavior from the phosphate solutions mentioned above, in that they show much more marked scintillations, so that when the voltage is reached at which the scintillations begin to contribute a significant share of the light, the brightness and efficiency curves each show a distinct bend, indicating that the light-emitting process occurring in

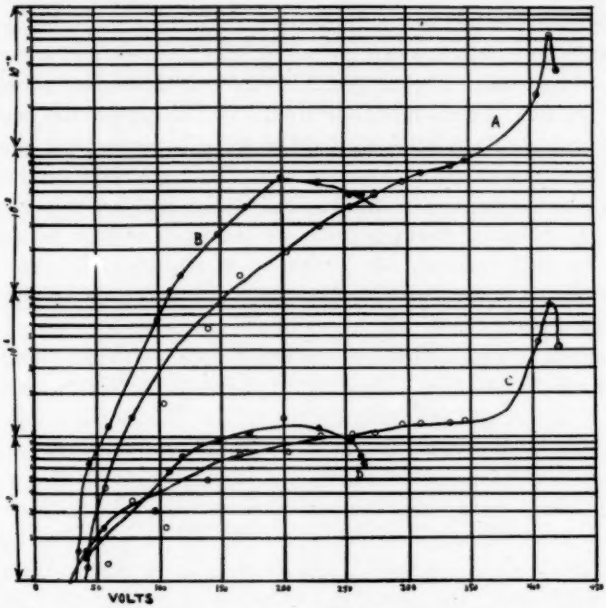

FIG. 3. *Effect of water-cooling aluminum anode in sodium pyrophsophate solution. A and B are brightness curves, C and D are efficiency curves; the ordinates are the same as on the preceding figures.*

the scintillations is a considerably more efficient process than that involved in the steady glow. This extremely interesting behavior is shown in Fig. 2, for ammonium borate; and Fig. 3 shows how, with water-cooled electrodes, a similar effect is obtained from sodium pyrophosphate solution. The effect of water-cooling is most pronounced in the case of this pyrophosphate solution. The curves illustrate experiments with electrodes cut from the same piece of metal, with the treatment as nearly alike as possible except for the water-cooling.

At sufficiently high voltages, the curves turn downward, the conditions rapidly becoming unstable as the voltage is increased. The instability seems clearly due to the heating; this conclusion is verified by a

set of tests made with the solution heated with a Bunsen burner. The heating reduced greatly both the brightness and efficiency.

In the course of this investigation, a study was made of the behavior of a large number of metals in typical Grignard solutions. Nine solutions, five of aliphatic and four of aromatic compounds, were studied, also solutions of $MgBr_2 \cdot 2(C_2H_5)_2O$, which resembles the Grignard compounds to a certain extent in its behavior. All these solutions are made up in anhydrous ether, since the substances are attacked and quickly destroyed by water or by oxygen. The chemi-luminescence accompanying the reaction of certain of these solutions with oxygen has been studied in considerable detail.[12] The earlier work had suggested that most metals would be found to behave similarly as regards the production of galvano-luminescence, but the present study discloses important differences in behavior between different groups of metals, as well as it verifies the differences already known to exist between different groups of solutions. It will be possible here only to summarize briefly the results from the very large number of observations made.

The aliphatic Grignard reagents studied were methylmagnesium bromide, methylmagnesium iodide, ethylmagnesium chloride, ethylmagnesium bromide, and ethylmagnesium iodide. The metals studied were copper, gold, magnesium, zinc, mercury, aluminum, tin, lead, tantalum, antimony, molybdenum, tungsten, iron, platinum. With this group of solutions, the metals giving the best glows are those in the second and third columns of the periodic table, i.e., Mg, Zn, Hg, Al. The metals in the first column are less active, and as one goes further to the right in the periodic table, the glows are fainter or non-existent, until with platinum no glow is found. The glow, when it appears, occurs at the anode. In all cases studied, no scintillations were found to accompany the glow in the ether solutions of Grignard reagents.

The aromatic Grignard reagents studied were phenylmagnesium bromide and phenylmagnesium iodide, of the mono-substituted phenyl derivatives, and para-chlorophenylmagnesium bromide and para-bromophenylmagnesium bromide, of the di-substituted compounds. This last compound frequently forms a double-layer solution; both layers were tested, but only slight differences were found. These aromatic compounds do give good glows with nearly all the metals tested, but

[12] Dufford, Calvert, and Nightingale, J. Am. Chem. Soc. *45*, 2058; 1923; J. Opt. Soc. Am. *9*, 405; 1924; J. Am. Chem. Soc. *47*, 95; 1925; Evans and Dufford, J. Am. Chem. Soc. *45*, 278, 1923; Evans and Diepenhorst, J. Am. Chem. Soc. *48*, 715; 1926; Dufford, J. Am. Chem. Soc. *50*, 1822; 1928.

mercury is an exception. The mono-substituted compounds show the glow at the anode; the bromine compound is more active, especially with the metals from the right hand side of the periodic table. It gives a a good glow with platinum. The solution of p-ClΦMgBr behaves similarly, but it gives a much weaker glow with platinum. The dibromobenzene derivative is remarkable in that it frequently shows a glow

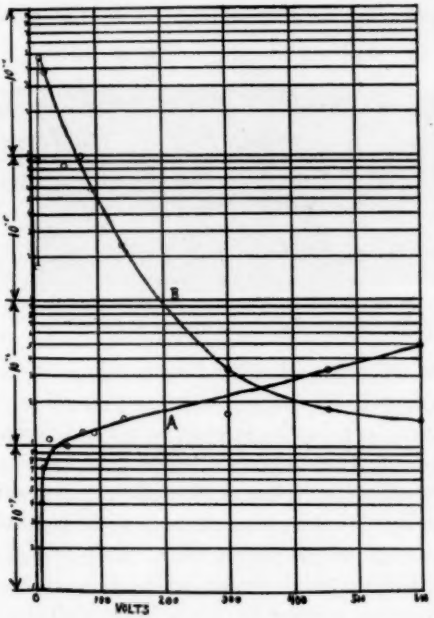

FIG. 4. *Brightness (A) and efficiency (B) of luminescence on platinum cathode in upper phase of ether solution of* $MgBr_2 \cdot 2(C_2H_2)_2O$. *The efficiency reached at 13 volts is the highest so far found for luminescence of this type.*

around the cathode, though an anode glow occurs in many cases too. It is possible that the effects from this solution may be affected by the presence of $MgBr_2 \cdot 2(C_2H_5)_2O$.

The solution of $MgBr_2 \cdot 2(C_2H_5)_2O$ gave results of particular interest. It, too, separates into two layers, both of which were studied. The solution used was prepared by letting ethylene bromide react with magnesium metal in dry ether. The lower layer, dark brown in color, is nearly saturated, and clear colorless crystals of etherated magnesium bromide form readily in it on standing. If this solution is electrolyzed, the glow ap-

pears suddenly, at the cathode, and apparently simultaneously a white film of etherated magnesium bromide appears on the electrode. The glow seems definitely associated with the film. The reason for the formation of the film seems to be that the local warming around the electrode boils off some of the ether, leaving the solution in the neighborhood supersaturated and ready to deposit the coating which is observed to form on the electrode. The film has been observed to grow to several millimeters thickness, without extinguishing the glow entirely. The

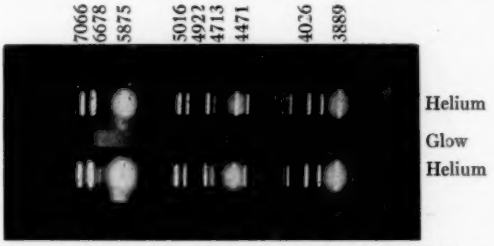

FIG. 5. *Photograph of spectrum of glow around aluminum anode in ammonium borate solution. (Compare with Fig. 6.)*

film is white and smooth, and redissolves in ether readily, giving a solution like the original. The upper layer of the solution is practically colorless and clear. Its behavior in electrolysis is different from that of any other solution tested. It gives a bright glow, which appears at the cathode, at unusually low voltages, the effect being well shown at ten volts. The brightness of the glow increases rapidly up to ten volts, but increases only very slowly at higher voltages, up to 600 volts. The efficiency curve for this material, shown in Fig. 4, is unlike any other such curve found, the peak coming at much lower voltages than for other similar cases. The maximum efficiency observed, $4.56\times10^{-4}\%$, at thirteen volts, is the highest on record for a case of galvano-luminescence. One would expect a film to form here, too, but none was observed. If it exists, it is too thin to be seen.

It is hoped that the results described may later be correlated with the photo-voltaic effect which occurs with these solutions, which is being investigated by one of the writers.[13]

It is a striking fact that in most cases of galvano-luminescence, the color of the light is bluish white, with almost no red present. The light from mercury anodes is an exception, the glow from this metal being

[13] Dufford, R. T., J. Phys. Chem. *34*, 1544; 1930, *35*, 988; 1931; Hammond, H. E., Phys. Rev. *35*, 998; 1930.

distinctly ruddy in many cases, though other colors are on record, for instance in the work of Bancroft and Weiser.[4] In a few cases, magnesium electrodes in Grignard solutions gave highly colored glows, in the present work, but this behavior is erratic, and the reason for it is not known. A photograph of the spectrum of the glow from aluminum in ammonium borate solution, reproduced in Fig. 5, shows the radiation distributed from about λ6500 to the violet and of the spectrum. The

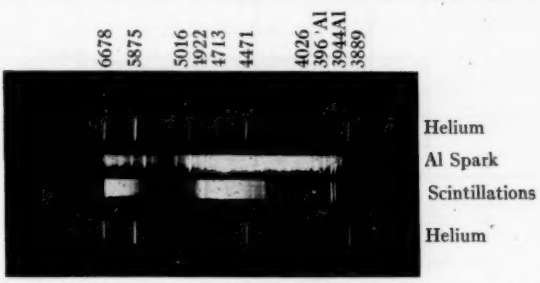

FIG. 6. *Photograph of spectrum of scintillations (with some light from glow also present) from aluminum anode in ammonium borate solution. (Compare with Fig. 5.)*

plate shows two maxima, probably due to the sensitivity minimum in the green which is shown by panchromatic plates. Visual observations confirm the fact that the spectrum consists of a single broad band. Forrest[11] has taken this spectrum as confirming the theory that the light comes from a film of oxygen gas which covers the anode. The writers are not convinced by this evidence, for the reason that spectra of this type are much less characteristic of oxygen than they are of the great majority of cases of chemi-luminescence[14] and of fluorescence and phosphorescence.

Another extremely interesting fact that came out during the present investigation, is that when the voltage applied to the electrolytic cell is plotted against the voltage applied to the photometer lamp used to measure the brightness of the glow in the electrolytic cell, the resulting graph is a *straight line*. Such a curve is shown in Fig. 7. This seems to indicate that the brightness of the galvano-luminescence, while of an entirely different order of magnitude from the brightness of the incandescent filament of the photometer lamp, must increase with applied voltage according to the same law as the brightness of an incandescent filament. So far as the writers are aware, no such fact has been shown

[14] Dufford, J. Opt. Soc. Am. *9*, 405; 1924, and Dufford, Nightingale, and Calvert, J. Am. Chem. Soc. *47*, 95; 1925.

to hold for a discharge through a gas. The indication is more nearly in the direction of a temperature effect. Such straight lines were obtained in a number of cases, both in borate and in phosphate solutions. However, the lines are straight only after the films have become formed; if a fresh metal surface is used, the curves rise more steeply at low voltages, but become practically straight at higher voltages. This latter observa-

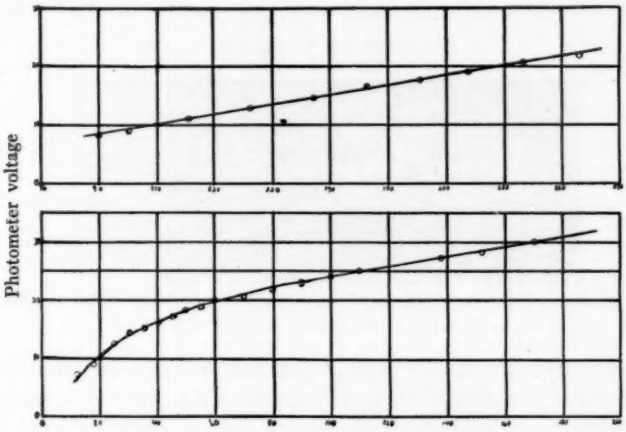

FIG. 7. *Variation of voltage on photometer lamp with voltage applied to luminescent cell. The upper curve is for a film which had been forming for six hours; the lower curve is for a freshly cleaned anode. (Aluminum anodes in ammonium borate solution.)*

tion would rule out any possibility of explaining the result by assuming errors due to reflected light, even if that possibility had not been guarded against in the experiments; but the brightness measured was certainly not perceptibly affected by reflected light from the photometer lamp, as could easily be demonstrated by turning off the cell current while the photometer lamp was kept on. The effect is due to the electrode film. McGregor[15] has suggested the possibility of using a reversible electrolyte, so that the thickness of the film on a rectifying electrode will remain constant. It would be interesting to see whether the relation found would still hold in such a case.

Further evidence against a gas-film theory is found in the fact that in certain cases the glow comes from the cathode instead of from the anode;

[15] McGregor, M. E., Nature, *125*, 128; 1930.

and also in the fact that it appears in certain solutions in which the liberation of oxygen seems very improbable.

The light from the scintillations, on the other hand, can be very definitely assigned to a gaseous source. A photograph of the spectrum of this light is shown in Fig. 6; it shows clearly a bright-line structure, in strong contrast with the glow spectrum shown in Fig. 5; and moreover, as may be seen from the comparison spectrum, the strongest pair of lines coincides with the strongest pair of lines in the spectrum of a condensed spark between aluminum electrodes in air. It follows that bright-line spectra from gaseous sources may appear under the conditions existing in these electrolytic cells; but the strong difference in the nature of the spectra, the great difference in the brightness of the light, and the difference in the efficiency of the emitting processes, all seem to corroborate the idea that the source of the steady glow is not a layer of gas. Of course, a layer of gas might conceivably exist, and still not be responsible for the glow.

SUMMARY

1. The study of galvano-luminescence has been extended to new solutions, and to new conditions in solutions previously investigated.

2. It is shown that water-cooling the anode may result in increased brightness and efficiency.

3. The spectra indicate that the scintillations have a gaseous source, while the source of the steady glow probably is not gaseous. Differences in brightness and efficiency seem to bear out this conclusion.

4. It is shown that under certain conditions the brightness of the glow increases with the applied voltage according to the same type of law as the brightness of an incandescent tungsten filament.

5. Systematic differences are found in the behavior of different groups of metals tested in nine typical Grignard solutions.

6. A solution of $MgBr_2 \cdot 2(C_2H_5)_2O$ gave a glow at unusually low voltages, and gave the highest efficiency so far found for a case of galvano-luminescence.*

* Since this article was written, other earlier work has come to the attention of the writers. J. Lifschitz, Proc. Loninkl. Akad. Amsterdam *26*, 561; 1923, describes and illustrates both types of spectra, and uses the name "volta-luminescence." Several other earlier papers are quoted.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA
THE REVIEW OF SCIENTIFIC INSTRUMENTS

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS

For the Period from January 1, 1930 to December 31, 1930

Cash on Hand, January 1, 1930		$ 5,618.27
Receipts:		
In account with the Optical Society of America (12 issues at $400.00 each)		4,800.00
In Account with Scientific Apparatus Makers of America		
Advertising		8,051.00
Miscellaneous Receipts:		
Subscriptions	$ 4,277.25	
Sale of back numbers	865.61	
Sale of copies of March 1929 issue	1.90	
Reimbursements	151.46	
Special amount for advertising the Helmholtz Translation	50.00	
Interest on Deposits in (1930)		
Ithaca Trust Company	181.57	
Ithaca Savings Bank	181.58	5,709.37
TOTAL		$24,178.64
Disbursements:		
Printer	$14,274.56	
Salaries and office expenses	5,709.55	
Miscellaneous	389.92	$20,374.03
Cash on hand, December 31, 1930		441.46
Amount deposited in interest accounts		3,000.00
Interest received on accounts (1930)		363.15
		$24,178.64

The above is a correct statement of accounts to the best of my knowledge and belief.

(Signed) F. K. Richtmyer, Business Manager

We, the undersigned, duly appointed to audit the account of the Journal of the Optical Society of America and The Review of Scientific Instruments at the close of business, December 31, 1930, hereby certify that we have examined the statement of receipts, and disbursements, the vouchers, check book and bank book and find them to agree with each other. We, therefore, certify that the above statement is a true statement of the accounts of the Journal of the Optical Society of America and The Review of Scientific Instruments as of December 31, 1930.

(Signed) Harley Howe
G. E. Grantham
Auditors

OPTICAL SOCIETY OF AMERICA

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS

For the Period from January 1, 1930 to December 31, 1930

Cash on Hand, January 1, 1930		$ 5,399.18
Receipts:		
Membership Dues Arrears (1929)	$ 254.40	
Membership Dues Current (1930)	4,926.09	
Membership Dues in Advance (1931)	2,960.30	
Subscriptions to Support of the Society	3,000.00	
Interest on Bank Balances	287.62	
Interest on Bonds	550.63	
Share of the Society in Journal Subscriptions	174.00	
Share of the Society from Advertisements in Journal	225.00	
Sales of Vols. I–V of Journal (Property of Society)	366.76	
Sale of Colorimetry Reports	27.50	
TOTAL RECEIPTS		$12,772.30
Total Receipts plus Cash on Hand, January 1, 1930		$18,171.48
Disbursements:		
To Journal of the Optical Society and The Review of Scientific Instruments as per Contract with Association of Scientific Apparatus Makers of America	$4,800.00	
Journal Subscriptions (320 @ $3.00 each)	960.00	
Printing and Stationery	329.05	
Postage and Telegraph in connection with Business of Society	88.35	
Postage on back numbers of Journal	6.98	
Traveling on Business of Society	57.38	
Clerical Expenses	178.63	
Fire Insurance Vols. I–V of Journal	6.80	
Labor and Transportation on Addressograph	110.47	
Sundry Expenses, Treasurer	15.39	
Advertising, Helmholtz Translation	50.00	$ 6,603.05
Purchase of Bonds for Investment	$7,653.28	
Accrued Interest on Bonds purchased	54.22	$ 7,707.50
Total Disbursements		$14,310.55
Cash on Hand, Dec. 31, 1930		3,860.93
Total Disbursements plus Cash on Hand, Dec. 31, 1930		$18,171.48

Investments:

$ 7000 Atchison, Topeka and Santa Fe Gen. 4's
$13000 Fourth Liberty 4¼'s
$ 500 Fourth Liberty 4¼'s (Frederick Ives Medal Endowment Fund)

I certify that the above report is correct to the best or my knowledge and belief.

ADOLPH LOMB
Treasurer

February 7, 1931

Adolph Lomb, Esq.
Treasurer, Optical Society of America:
Dear Mr. Lomb,

In accordance with your request we have audited the treasurer's accounts of the Optical Society of America for the twelve months ending December 31, 1930; and we hereby certify that the treasurer's official reports of receipts, disbursements and investments for the year 1930 is correct in every detail, as shown by bank statements, vouchers, etc.

Yours truly,
JAMES P. C. SOUTHALL
C. L. TRELEAVEN

La Mesure des Rayons de Courbure des Surfaces Spheriques employees en Optique. By Albert Arnulf. Éditions de la Revue d'Optique Théorique et Instrumentale, Paris, 1930.

To make a precision optical component complying with the specifications of the designer it is necessary that the index of the optical glass be accurately measured and that means be available for determining the radii of curvature of the surfaces. It is to the solution of this latter problem that this volume is addressed. Dr. Arnulf discusses the usual methods of measuring curvature and in addition has presented many new methods which, in general or for specific applications, possess advantages in convenience, accuracy or precision over the accepted methods. The author is chief of the "Travaux Pratiques" at the Optical Institute and the great number of original contributions in this volume presents the results of many years work dedicated to improving and making known the technique of optical construction. In most cases finished instruments suitable for the routine application of the methods have been built and the methods which are presented are those which have met the test of practical application and been found satisfactory. There is a general discussion of each method, specifications and photographic reproductions of the apparatus which has been built for its application and a critical treatment of the errors to which the method is subject.

The portion of applied optics covered by this book is small in scope. Nevertheless the subject is one of strategic importance and the thorough and comprehensive manner in which it is treated makes the book very much worth while. In publishing this volume Dr. Arnulf has rendered an important service to the optical industry of the world. It is much to be desired that other books be published dealing with the other similar problems which arise in connection with optical manufacture.

I. C. GARDNER

Applied Photography, a New Journal for Industry Noteworthy examples of photography as used for various business purposes fill the pages of *Applied Photography*, a new magazine which made its appearance May 1. The magazine is sponsored by the Eastman Kodak Company as part of an extensive program to assist industrial and business firms in applying photography effectively in research, manufacturing, advertising and sales work.

The scope of the new magazine includes the industrial applications of still and motion pictures, photomicrography, radiography, and other forms of photography.

Each issue presents a different business objective, and illustrates how photography can aid in attaining it. The first issue deals with the question

of obtaining photographs for advertising and sales purposes—photographs showing the performance or utility of products. Among the illustrations chosen as examples are many noteworthy photographs which have been used in selling tractors, metals, motor trucks, protective coatings, railway equipment, musical instruments, tools, anesthetics, and arc welding.

The mailing list for the new Eastman magazine is open to executives in charge of advertising, sales, research, and factory production, and will be so classified that persons on the list will receive, without charge, such issues of the magazine as bear directly on their industry or profession. With this method of distribution, the arrival of a copy of *Applied Photography* is a signal that useful information is at hand. A subscription list will also be maintained for others wishing to receive the magazine regularly.

Business executives should find *Applied Photography* an invaluable pictorial reference book, which will keep them informed of new developments in photography as applied to manufacturing and merchandising problems.

The editor of the journal is R. C. Tuttle, Eastman Kodak Company, Rochester, N. Y.

An Introduction to Applied Optics, Vol. 1. General and Physiological. By L. C. Martin, D. Sc., A. R. C. S., D. I. C. Pp. vii+324, 195 Figs. Isaac Pitman & Sons, $6.00.

This work is intended to occupy a position intermediate between advanced mathematical treatises and the rather superficial discussions typical of many textbooks on the subject. It is the intention to cover the general aspects of applied optics without going into detailed methods of design. The work is apparently to be completed in two volumes and since only Vol. 1 is now available it is difficult to say just how thoroughly the subject will be covered. Assuming however, that the discussion in this portion of the work is representative of the presentation intended for the remainder of the work it is safe to say that it will be a worth while addition to the literature on the subject.

Briefly summarizing the content of Vol. 1 to indicate the scope of the book: elementary theory, general theory of optical systems, the optical image and its defects, physical and physiological optics, optical glass and the production and testing of lens systems, and spectacles are the main topics discussed. The presentation is so handled as to lead one from elementary discussions to the more complex problems in a very satisfactory manner. The mathematical work is clear, adequate and as simple as the scope of the work permits.

The 48 page chapter on spectacles discussing the common defects of the eye and their correction while necessarily brief, covers the subject in a manner quite satisfactory to anyone but a specialist. If the discussions of other instruments in the forthcoming Vol. 2 handle the subjects in an

equally adequate yet concise manner one could even now recommend not only Vol. 1, but the entire work.

R. D. WYCKOFF

Handbuch der Spectroscopie VII, 2nd Number, pp. 500–750. H. Kayser and H. Konen, S. Hirzel, Leipzig, 1930.

When Kayser's *Handbuch der Spectroscopie* was completed in six massive volumes it was a critical treatise which embraced all knowledge on this subject, and might be expected to endure indefinitely with occasional slight revisions. Since the first volume appeared in 1900 and the sixth in 1912, Professor Kayser immediately began revising Vol I, which was in fact being reprinted in 1914 when it was stopped on account of the war. After this long and wasteful struggle, it was not possible to continue with a complete revision of the Handbuch, but Professor Kayser decided to extend the last two volumes dealing with the emission spectra of the chemical elements. Whereas Vol. I dealt principally with spectroscopic methods and apparatus which have seen little change or improvement in the last two decades, it is just this period which has witnessed one of the greatest developments in the history of Science, namely, the quantum interpretation of atomic and molecular spectra.

The interest in spectroscopy increased by leaps and bounds and so did the literature. It became increasingly difficult for workers in spectroscopy to keep abreast with the publications, and an extension of the Handbuch by Kayser and Konen was most welcome. But the economic conditions following the war made it impossible to proceed regularly with the work; the printing was actually begun in 1921 and yielded by 1923 a book of 500 pages which was issued as Vol. VII, No. 1. This dealt with the spectra of 20 elements from argon (A) and iron (Fe) inclusive. Then another aggravating delay occurred and it is only now that Vol. VII, No. 2 has been released. It is somewhat disappointing that this part deals with only 10 elements, gallium (Ga) to iridium (Ir), and reviews the subject matter only to 1927. The plan is to publish a third number bringing the first two both up to date, and then proceed with numbers dealing with the remaining 60 elements the literature on which has grown enormously in 20 years. The accelerated rate at which spectroscopic papers have been accumulating is seen by comparing this last number with Vol. V. Hydrogen, for example, had, in Vol. V, 187 literature references dating from 1851 to 1909, but according to Vol. VII, No. 2, it had a total of 736 in 1927. Helium had 121 in 1909 but in 1927 it had 390. Mercury had 144 in 1909 but 518 in 1927. In many cases the number of published papers now greatly exceeds the number of spectrum lines characteristic of an element, and it is quite hopeless for the individual worker in spectroscopy to find it and review it by himself. Thus, even if the extended Handbuch had no other virtue than that of containing a

reasonably complete bibliography of the literature on experimental spectroscopy it would still be a worth while undertaking. Certainly all spectroscopists will appreciate the efforts which Kayser and Konen are making to facilitate further progress in this branch of Science.

WILLIAM F. MEGGERS

Veröffentlichungen des Wissenschaftlichen Zentral-Laboratoriums der Photographischen Abteilung Agfa—Band I. 1930.

This begins a series of annual compilations of technical investigations conducted by the German photographic concern Agfa. The first volume contains only work which has been published in other places, but in general some papers will appear which will not have been published elsewhere. Also from time to time there will appear collected references on important photographic problems.

The present volume is composed of eleven articles. One article on the present theories of the latent image, two articles on spectral sensitometry, and one on a three dimensional method of representing sensitometric properties of a photographic emulsion, comprise the part on the more theoretical aspects of photography. Several of articles are concerned with applied photography in such fields as infrared photography, testing of sound film, and stereoscopic x-ray pictures. Two papers on cellulose and cellulose derivatives complete the list.

The photographic world has needed more publications entirely devoted to photographic problems. The Agfa annual will serve a very useful purpose in helping to keep important photographic knowledge collected and its editors are to be commended for their efforts.

M. E. RUSSEL

Erythema Due to Ultraviolet Radiation (Erratum).—By E. Q. Adams, B. T. Barnes and W. E. Forsythe. In the caption to Fig. 6, (J.O.S.A. *21*, 213; 1931) the statement is made that exposure is in the same units as in Fig. 5. To make this statement true the scale of ordinates should be reduced 10-fold, extending from .001 to 100. This change will not affect any of the tables or figures later in the article, as in each case the effect at some stated degree of erythema has been placed equal to 100 percent or unity. The authors are indebted to Mr. L. L. Holladay, of the Lighting Research Laboratory, for this correction.